SERIES SPECTRA OF TWO-VALENCE-ELECTRON ATOMS OF BORON (B_{II}) AND CARBON (C_{III})

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Abstract

Series spectra of B_{II} and C_{III}.—By methods previously reported in the identification of lines in the extreme ultraviolet, 13 lines in addition to the pp' group of B_{II} have been identified, completing the classification of all lines known to be due to B_{II}. Taking the $4f$ level as 27800 (probably correct to within 200 frequency units), the following term values were obtained for B_{II}: $3s$, 72930.8; $4s$, 36655.5; $2p_1$, 165343.9; $2p_{2,3}$, 165362.7; $3p_1$, 59006.5; $3p_{2,3}$, 59010.0; $3d$, 52054.2; $4d$, 28640.4; $5f$, 17795.7; $2S$, 194325.9; $3S$, 66665.1; $2P$, 120929.4; $3D$, 48410.3. In the case of C_{III}, 8 lines in addition to the pp' group were identified, and taking the $4f$ level as 62600, the following term values were obtained for C_{III}: $3s$, 146197.2; $2p$, 331939.2; $3p_1$, 124685.8; $3p_2$, 124698.6; $3p_3$, 124704.1; $3d$, 114387.2; $2S$, 375463.1; $2P$, 273111.0.

Progression of frequency separations and of screening constants for regular doublets for Li to O is shown in Table VI, for one to six valence electrons. The separation $(2p_2-2p_1)$ or $(2p_3-2p_1)$ regularly decreases and the constant s regularly increases, for a given element, with the number of valence electrons, irrespective of the fact that both doublets and triplets are involved.

1. Identification of B_{II} Lines

THE term-values of the stripped, or one-valence-electron, atoms of boron (B_{III}) and carbon (C_{IV}) have recently been worked out and published.[1] In the case of two-valence-electron atoms of these elements we have observed and published the characteristics of their pp' groups,[2] and have thus fixed with accuracy the frequency separations of the three $2p$ levels, viz. $2p_1$, $2p_2$, $2p_3$.

But as soon as these separations are known it becomes possible to identify the boron lines which arise from jumps into these $2p$ levels. Thus the separation between $2p_1$ and $2p_3$, i. e., the total width of the triplet, is actually the distance between the second and the last components of the pp' group, numbering from the short wave-length side. This was found from the pp' plates to be 22.8^{-1} for B_{II}.

The first member of the diffuse series of B_{II} $(2p-3d)$ ought to be located at a wave-length a little larger than the corresponding line of stripped boron (B_{III}) which was before found at λλ677.01, 677.16.

[1] Bowen and Millikan, Proc. Nat. Acad. **10**, 199 (1924), and Nature **114**, 380 (1924).
[2] Towen and Millikan, Phys. Rev. **26**, 150 (Aug. 1925).

The only strong line on our plates in approximately this position is the line the wave-length of which we had published as 882.3A. In this region the foregoing separation would amount to but 0.18A. Since the p_2p_3 separation was less than a third of this we could not hope to resolve all three of the $(2p-3d)$ lines but could expect to obtain a resolution that would bring to light a doublet with a separation equal to the distance of p_1 from the center of gravity of p_2 and p_3.

We accordingly sought to obtain a spectrogram of the fifth and sixth orders of the line 882.3A. In both these orders it appeared as a doublet, as predicted, with a frequency separation of 18.3 cm^{-1}. Since this is definitely different from the characteristic separations of both B_I and B_{III} it can only be due to B_{II}. Again, the $(2p-3s)$ line of B_{II} must reveal the same separation as the foregoing but should have a slightly longer wave-length. Our next strong line, namely that at λλ1081.88, 1082.10, showed as a doublet in the fourth and fifth order spectra with a measured separation of 19.3 cm^{-1}, in agreement within the limits of error with the foregoing.

The next jump most likely to occur is the $(3d-4f)$. This jump is between two remote circular orbits and its value may be computed roughly by multiplying the corresponding line for hydrogen by four. This gave λ4688. The only unidentified line of any strength in this region was that at λ4122.99, which was accordingly taken as the line sought.

The $4f$ level for B_{II} would have a frequency value, if it were completely hydrogen-like, of $109732/4=27433$. The corresponding value for two-valence electron aluminum (Al_{II}), which is certainly less perfectly screened than B_{II}, is 28440. The $4f$ term-value for B_{II} had to lie between these limits and was taken as 27800, the uncertainty being not more than two or three hundred frequency units. With the aid of this starting point and the foregoing lines the $3d$, $2p$, and $3s$ levels were at once obtained as shown in Table I. The line $(3s-3p)$ has not yet been observed, but a fairly accurate prediction as to its frequency can be made from the frequency of the corresponding line in C_{III} and the progression of the Mg_I to S_V series.[3] By taking this line as having a frequency 13920, the $3p$ level was obtained from this frequency and the already-determined $3s$ level. The jump $(3p-4s)$ was found by looking for another doublet having the $3p$ separations. This was found at λλ4473.37, 4474.08, and this fixed the $4s$ level shown in the table.

[3] Bowen and Millikan, Phys. Rev. **25**, 594 (1925).

The B_{II} singlet series was worked out as follows. By comparison with the $3S-3P$ lines of the series Mg_I to Cl_{VI} and the already located $2S-2P$ line of Be_I,[4] viz., 2348.70, it was seen that $2S-2P$ for B_{II} should fall at about 1400A. The only very strong line in this region, in fact the strongest unidentified boron line below 3000A, was 1362.46A. This could scarcely be any other than $2S-2P$. The next strongest

TABLE I

Series lines for B_{II}

Int.	λ(I.A., vac.)	ν	Δν		Term values	
0	731.46	136712.9		$2p-4d$	$3s$	72930.8
3	882.55	113308.2		$2p_{2,3}-3d$	$4s$	36655.5
			> 18.3			
3	882.69	113289.9		$2p_1-3d$		
					$2p_1$	165343.9
3	1081.88	92432.1		$2p_{2,3}-3s$	$2p_{2,3}$	165362.7
			> 19.3			
3	1082.10	92412.8		$2p_1-3s$	$3p_1$	59006.5
					$3p_{2,3}$	59010.0
8	1362.46	73396.5		$2S-2P$		
3	1378.95	72519.1		$2P-3D$	$3d$	52054.2
4	1623.66	61589.2			$4d$	28640.4
4	1623.86	61581.7				
5	1624.08	61573.2		pp' group		
4	1624.25	61567.0			$4f$	27800.0
4	1624.46	61558.9				
					$5f$	17795.7
5	1842.83	54264.3		$2P-3S$		
2	2918.98	34258.5		$3d-5f$	$2S$	194325.9
10	3452.33	28965.9		$2S-2p_2$	$3S$	66665.1
6	4122.99	24254.2		$3d-4f$		
					$2P$	120929.4
1	4473.37	22354.5		$3p_{2,3}-4s$		
			> 3.5			
1	4474.08	22351.0		$3p_1-4s$	$3D$	48410.3

lines to be expected were the $(2P-3D)$ and the $(2P-3S)$, the former of which should have the shorter wave-length. The only unidentified boron lines below 3000A, were[5] now λ1378.95 and λ1842.83, the first of which should therefore be $(2P-3D)$ and the second $(2P-3S)$. This fixes every known boron line of any strength except the familiar

[4] Paschen and Götze, Seriengesetze etc., p. 71.

[5] The line λ1378.95 did not appear in our original list of boron lines (Phys. Rev. **23**, 7, 1924) because, with the resolution then used it was not separated from the strong aluminum line at λ1379.7. With our present high-resolution the two lines are very easily seen to be distinct.

and exceedingly powerful line at $\lambda_{vac}=3452.33$ which, in conformity with the behavior of all two-valence electron systems is $(2S-2p_2)$. This connects the singlet and triplet systems, the latter of which have been worked out above; i. e. $2p_2$ being known, this last line fixes the value of $2S$, and from this all the other singlet levels come out at once from the foregoing relationships with the values given in Table I.

The present work then completes the identification of all the known boron lines of any intensity and the classification into series of all the lines due to B_{II} and B_{III}.

2. Method of Identification of C_{III} lines

One of the chief contributions of our development of hot-spark spectrometry to the identification of spectral lines has arisen from the fact that with these hot sparks we have been able to obtain for comparisons in the optical region a long series of atoms of varying nuclear charge but of like electronic structure and have found through such comparisons that such series follow the Moseley law quite as well in the field of optics as in the field of x-rays. The analytical expression of this law is

$$\frac{\nu}{R}=\left(\frac{Z-\sigma}{n}\right)^2 \tag{1}$$

in which ν is the energy of the orbit expressed in terms of a frequency, Z the atomic number, σ the screening constant and n the total quantum number. We have already pointed out that the frequency ν' of a spectral line due to an electron jump between two such orbits which have different screening constants σ_1 and σ_2 respectively must be given, with entire generality, by

$$\frac{\nu'}{R}=\left(\frac{Z-\sigma_1}{n_1}\right)^2-\left(\frac{Z-\sigma_2}{n_2}\right)^2 \tag{2}$$

or

$$\frac{\nu'}{R}=\frac{(n_2^2-n_1^2)Z^2-2(n_2^2\sigma_1-n_1^2\sigma_2)Z+n_2^2\sigma_1^2-n_1^2\sigma_2^2}{n_1^2\,n_2^2} \tag{3}$$

an equation which shows, as previously pointed out, that when, and only when n_2 is equal to n_1 and σ_1 and σ_2 are independent of Z, do the frequencies ν' progress linearly with atomic number Z, i. e., follow the irregular doublet law.

In seeking to use these relations for the prediction of the positions of the spectral lines of C_{III} we observe first that the strongest C_{III} line to be expected at all is the first term of the principal series of singlets,

viz. $(2S-2P)$ and, since for this line $n_2=n_1$ and σ_1 and σ_2 may be expected to be independent of Z, there should be here a linear progression of ν' frequencies with atomic number, a prediction which we have always found experimentally verified in the case of all lines that are due to jumps between orbits of the same total quantum number. Table II gives in its first two rows the frequencies of this line for two-valence-electron beryllium (Be_I) and boron (B_{II}) and enables us definitely to locate $(2S-2P)$ for C_{III} at approximately $73000+30000=103000$, which corresponds to $\lambda 971$. This identifies the very strong carbon line 977.02 as the $(2S-2P)$ line of C_{III}, for our plates taken with high resolution reveal this as the only singlet carbon line of any strength within a hundred angstroms of the predicted wave-length.

TABLE II

Irregular doublets, $2S-2P$

	Frequency	Diff.
Be_I	42565.1	
		30831.4
B_{II}	73396.5	
		28955.6
C_{III}	102352.1	

The next strongest C_{III} lines should be $(2p-3d)$ and $(2p-3s)$. It is, however, impossible to locate them by means of the irregular doublet law, since, n_2 being here different from n_1, this law can no longer hold. Eq. (3), however, is of general validity and gives the actual variation of ν' with Z if only σ_1 and σ_2 are not functions of Z, as has been shown to be the case by the observed linear relation between ν' and Z when $n_1=n_2$.

Also (3) may be written

$$\nu'-RZ^2(n_2^2-n_1^2)/n_1^2n_2^2=CZ+D \qquad (4)$$

where C and D are constants so long as we are considering a given sort of electron-jump, i. e., a given set of values of n_2, n_1, σ_1, and σ_2. The quantity on the left will then show a linear progression with Z.

To transform this expression into one slightly more convenient for use we substitute $(Z-A)$ for Z and get

$$\nu'-R(Z-A)^2(n_2^2-n_1^2)/n_1^2n_2^2=C'Z+D' \; . \qquad (5)$$

The left side is again a quantity which varies linearly with Z and from which ν' may be predicted for any value of Z as soon as any two other values have fixed C' and D'. For the case in hand $n_2=3$, $n_1=2$ and hence

$$R(n_2^2-n_1^2)/n_1^2n_2^2=109732(9-4)/[9\times 4]=15240.55 \; . \qquad (6)$$

We are here dealing with the progression with atomic number in the

frequency of a particular line found in the spectra of beryllium, boron, and carbon. Hence to make $(Z-A)$ conveniently small we shall take $A=3$. Then with the use of Paschen and Götze's value of ν' for $2p_2-3d$ in beryllium (Be_I) and our own value, determined above, of the same line in B_{II} we obtain the first two numbers under column 2, Table III. The first two numbers of column 3 are obtained by subtracting 1 and 4 times 15240.55 respectively from these two frequencies in column 2. The numbers in column 3, which now represent the left side of Eq. (5), should progress linearly with Z, and hence the difference between them (first number in column 4) added to the second in column 3 should give the left side of Eq. (5) for C_{III}. By adding 9×15240.55 to this we obtain the frequency of $2p-3d$ for C_{III}. The result thus obtained is found to fall within 500 frequency units, or about 1 angstrom, of the strong carbon line at λ459.7. The data given under C_{III} in Table III are the *observed* values corresponding to this line and show how nearly linear is the actual progression.

TABLE III

Progression with atomic number of the frequency of $(2p_2-3d)$ and $(2p_2-3s)$

		ν	$\nu-(5/36)(Z-3)^2R$	Diff.
$2p_2-3d$	Be_I	40075.13	24834.58	
				27511.42
	B_{II}	113308.2	52346.0	
				28041.0
	C_{III}	217552.	80387.	
$2p_2-3s$	Be_I	30100.88	14860.33	
				16609.57
	B_{II}	92432.1	31469.9	
				17107.1
	C_{III}	185742.	48577.	

By precisely the same procedure, using the $(2p-3s)$ frequencies for Be_I and B_{II}, we obtain the lower half of Table III and identify the strong carbon line λ538.4 as $2p-3s$ for C_{III}.

The next strong line to be sought in C_{III} would naturally be $(3d-4f)$ and since this is a jump between two fairly remote circular orbits it should be approximately hydrogen-like and hence have an approximate frequency 9 times, or a wave-length one-ninth of, the value for the corresponding line (λ18751) in hydrogen. The result is λ2083, which identifies with sufficient accuracy the strong carbon line at 1930.98 as $(3d-4f)$ for C_{III}.

The carbon triplet at λλ4648.70, 4651.46, 4652.65, long ago found in the hottest stars (O type stars), obtained also in the laboratory by

Merton in 1915,[6] has already been classified as belonging to C_{III} because it does not appear in the arc spectrum, and, being a triplet, can therefore not belong to any stage of ionization of carbon other than C_{III}. It is here for the first time identified as $3s-3p$ by the fact that its position is about right[7] for $3s-3p$ and by the further fact that the separations of its components require it to be a line of a principal series and there is no other principal series triplet of suitable intensity.

The very strong carbon line at 2297.59 we identify as $2S-2p_2$, first by elimination—all of the other C_{III} lines that may be expected to be strong have already been identified and this line must belong to C_{III} since it is definitely a spark line and is not in Fowler's group of C_{II} lines; second, roughly by position—the $2S-2p_2$ line in B_{II} being at λ3452.33, the corresponding line in C_{III} may be expected to be somewhere between 2000 and 3000A; third, by its characteristics—this line comes out very easily for so high a stage of ionization and this is characteristic of the $2S-2p_2$ line wherever it appears.

TABLE IV

Series lines for C_{III}

Int.	λ(I.A., vac.)	ν	Δν		Term values	
6	459.7	217552.		$2p-3d$	$3s$	146197.2
7	538.4	185742.		$2p-3s$		
					$2p$	331939.2
12	977.02	102352.1		$2S-2P$		
					$3p_1$	124685.8
4	1174.96	85109.0			$3p_2$	124698.6
4	1175.31	85084.2			$3p_3$	124704.1
5	1175.72	85054.0		pp' group		
4	1176.03	85031.6				
4	1176.40	85005.1			$3d$	114387.2
7	1930.98	51787.2		$3d-4f$		
					$4f$	62600.
10	2297.59	43523.9		$2S-2p_2$		
3	4648.70	21511.4		$3s-3p_1$	$2S$	375463.1
			>12.8			
2	4651.46	21498.6		$3s-3p_2$		
			> 5.5		$2P$	273111.0
1	4652.65	21493.1		$3s-3p_3$		

We have sought without success on our plates for the other singlet lines of C_{III} which might be expected to be strong, such, for example, as $2P-3D$ and $2P-3S$. This failure might possibly raise some question

[6] Merton, Proc. Roy. Soc. **91**, 498, (1915).

[7] $(2p-3d)-(2p-3s)=3s-3d=31810$ (see above), and $3s-3p$ should be about 2/3 of $3s-3d=21000$ cm^{-1} or at λ 4762.

about some of the other identifications, although it is in keeping with the fact that Fowler has been unable to find the corresponding lines in Si_{III}.

The starting point for obtaining the series of C_{III} levels from the foregoing lines was taken, as in the case of B_{II}, as close to the theoretical hydrogen-like value for $4f$. This hydrogen-like value for C_{III} should be $109732 \times (9/16) = 61724.3$. We arbitrarily took, as in the case of B_{II}, a value a trifle higher than this, namely 62600, and then obtained at once from this and the foregoing line-frequencies the term-values given in Table IV.

TABLE V

Comparison of term values

	$N=$ / $R/N^2=$	2 / 27433.0	3 / 12192.3	4 / 6858.3
s	B/4	.....	18232.7	9163.9
	C/9	.....	16244.1	
p_1	B/4	41336.0	14751.6	
	C/9	36882.1	13854.0	
d	B/4	.....	13013.6	7160.1
	C/9	.....	12709.7	
	B/4	.....	.....	6950.
	C/9	.....	.....	6955.6
S	B/4	48581.5	16666.3	
	C/9	41718.1	.....	
P	B/4	30232.4	.....	
	C/9	30345.7	.....	
D	B/4	.....	12102.6	

Table V is added to conform with the general scheme of comparison of term-values that we have heretofore used, following Paschen and Fowler.

3. Effect upon the Force Field within the Atom of the Successive Addition of Electrons to the Valence Shell

We have added a further Table VI for the sake of exhibiting even more strikingly than we have heretofore done, first, the systematic progression of the value of the screening constant s of the regular-doublet law as each new electron is added to the valence shell, and, second, the fact that the triplets behave precisely as do the doublets in systems of like electronic structure and varying nuclear charge.

The upper half of the table gives the $(2p_2-2p_1)$ doublet-separations in the first, third, and fifth columns, for one, three, and five electron systems, respectively, and the $(2p_3-2p_1)$ triplet separations in the second, fourth and sixth columns, for two, four, and six electron systems. For the two-valence electron systems these separations are obtained from the pp' groups. The lower half of the table gives the values of the screening constant s as computed from the regular doublet law as outlined in Physical Review **24**, 209 (1924). The table shows very

TABLE VI

Frequency separations and screening constants for regular doublets and triplets

Electrons =	1	2	3	4	5	6
	$(2p_2—2p_1)$	$(2p_3—2p_1)$	$(2p_2—2p_1)$	$(2p_3—2p_1)$	$(2p_2—2p_1)$	$(2p_3—2p_1)$
Li	.338					
Be	6.61	3.02				
B	34.1	22.8	15.55			
C	107.4	79.1	66.76	46.8		
N	259.1	204.1	179.3	132.2	85.3	
O	.....	459.5	398.4	309.0	....	224.0
	Screening constant $s=Z-\sqrt[4]{\Delta\nu/.365}$					
Li	2.019					
Be	1.937	2.304				
B	1.884	2.189	2.445			
C	1.858	2.163	2.332	2.635		
N	1.838	2.137	2.292	2.638	3.090	
0	.....	2.043	2.252	2.606	.....	3.023

beautifully the effect upon the force-field about the nucleus of the successive addition up to six of each new valence electron to the valence shell. The progression is at least qualitatively quite such as is to be expected from the successive introduction into the atom of six point charges each endowed with a coulomb field.

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